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<p>(21) International Application Number: PCT/GB89/00042</p> <p>(22) International Filing Date: 18 January 1989 (18.01.89)</p> <p>(31) Priority Application Number: 8801827</p> <p>(32) Priority Date: 27 January 1988 (27.01.88)</p> <p>(33) Priority Country: GB</p> <p>(71) Applicant (<i>for all designated States except US</i>): JCT CONTROLS LIMITED [GB/GB]; Brook Road, Wimborne, Dorset BH21 2BH (GB).</p> <p>(72) Inventors; and</p> <p>(75) Inventors/Applicants (<i>for US only</i>) : ELLIS, Richard, Margrave [GB/GB]; 26 Ramsbury Close, Blandford Forum, Dorset DT11 7UP (GB). HOULSTON, John, Francis [GB/GB]; Silver Glen, Rushall Lane, Lytchett Matravers, Poole, Dorset (GB).</p>		<p>(74) Agent: HULSE & CO.; Cavendish Buildings, West Street, Sheffield S1 1ZZ (GB).</p> <p>(81) Designated States: AT (European patent), AU, BE (European patent), BR, CH (European patent), DE (European patent), DK, FR (European patent), GB (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), NO, SE (European patent), US.</p> <p>Published With international search report. With amended claims.</p>	
<p>(54) Title: ELECTROCHEMICAL PROCESSES</p> <p>(57) Abstract</p> <p>A method of operating an electrochemical process comprises the application of at least two independently-controlled voltages in alternation, the equipment comprising at least two independently controlled electrical power sources (7, 8) and switching means (9) for applying them in alternation to a cell (4) in which are suspended a workpiece (2) and another electrode (3). If more than two independently controlled voltages are utilised they will be applied cyclicly. Preferably, one of the two or more voltages will be reversed, and may be pulsed, and the electrolyte preferably comprises at least two organic additives, at least one being a polariser the effects of which are inhibited by reverse voltages, and the other being a depolariser that is preferentially adsorbed.</p>			
<p>Voltage</p> <p>+</p> <p>0</p> <p>-</p> <p>Time</p>			

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ELECTROCHEMICAL PROCESSES

This invention relates to improved means for carrying out electrochemical processes, particularly electrodeposition.

The basic arrangement for a typical electrodeposition process is shown diagrammatically in Figure 1(a) of the accompanying drawings, in which a source of electrical power is shown at 1. This is most commonly a transformer-rectifier but may alternatively be a battery or a rotary generator. Means for varying the output voltage are provided. The current source 1 is connected to a workpiece 2 and another electrode 3 which are suspended in a cell or bath 4 of electrolyte solution forming an electrolytic cell.

In a known technique for operating the process, termed "Periodic Reverse Plating", a reversing switch unit 5 is interposed between the power source 1 and the cell 4. The unit 5 may be a number of switches operated mechanically, appropriate electromechanical relays or solid state devices. The unit 5 operates at intervals, producing the effect shown in Figure 1(b), which is a graph of the voltage applied to the cell against time. The normal voltage V is replaced at intervals by the same voltage in the opposite sense.

Obviously, to obtain a net plating effect, the total time for which forward (+) voltage is applied must be greater than that with reverse (-) voltage.

Another known technique is "Pulse Plating". The basic arrangement is shown diagrammatically in the accompanying Figure 2(a). It is the same as that of Figure 1(a), except that a pulsing unit 6 replaces the switch unit 5. The unit 6

periodically interrupts one or both of the connections between the power source 1 and the cell but does not reverse them. This produces the effect shown in Figure 2(b), again a graph showing the relationship between voltage applied to the cell and time. Normally a fairly high frequency is required, up to 5,000 cycles per second or more and the only suitable construction for the unit 6 is a solid state device, such as an array of field-effect transistors which may be controlled by a microprocessor.

Pulse plating can have various beneficial effects. It can refine the crystal structure of the deposit, reduce its porosity or stress, or improve throwing power. The facility for varying the voltage of the source 1 can be retained and further control of the process is usually provided by adjustment of the frequency at which the unit 6 "chops" this supply or the proportion of each cycle for which it is "on" or "off", that is, the "mark-space ratio".

It is yet further known to combine the functions of periodic reverse and pulsing in one control unit, so that desired effects such as shown in the accompanying Figure 3 may be produced, in which the voltage is reversed for periodic short intervals and both forward and reverse supplies may be pulsed, but the input supply voltage, though variable at the source, is the same in both senses.

It is true that, by pulsing a supply and altering the mark-space ratio of pulsing, the mean output voltage may be changed. By the use of a smoothing circuit with capacitors and/or inductors a uniform direct current may then be obtained. This is an effective means of providing a

variable-voltage direct current supply as required for the unit 1 of Figures 1 or 2, reversal or pulsing being subsequently applied as required. It is important to distinguish such a supply system from pulsing as such, the action of which depends on the square (approximately) wave form of the voltage which must not then be smoothed or the effect will be destroyed.

It must now be noted that most electrochemical processes are critically dependent on the applied voltage. For example, any pair of dissimilar metals immersed in an electrolyte will generate an inherent voltage and little or no current will flow in the opposing direction until a voltage greater than the inherent voltage is applied. On the other hand, excessive voltage can produce undesirable effects. It is thus often required to control the voltages in the forward and reverse directions independently. No provision for this is available in any arrangement previously known.

It must also be noted that electrolytes used for electrodeposition purposes generally contain, apart from appropriate metal ions, organic additives which are there for the specific purpose of modifying the structure and/or brightness of the metal deposit. These additives are usually adsorbed or diffused onto the deposit surface and cause changes in deposit structures some of which are not always desirable.

The object of the invention is to improve the performance of an electrochemical process, more particularly - but not exclusively - electrodeposition.

According to the present invention, a method of

operating an electrochemical process comprises the application of at least two independently-controlled voltages in alternation. It will be evident that if more than two independently-controlled voltages are utilised they will be applied cyclicly. Preferably, one of the two or more voltages will be reversed. Alternatively one of the voltages may modulate the other or another voltage. One or each voltage may be pulsed.

Another aspect of the present invention is the provision of equipment for operating an electrochemical process comprising at least two independently-controlled electrical power sources and switching means for applying them in alternation. Alternatively the switching means could be adapted to apply more than two independently-controlled voltages cyclicly. Preferably, the switching means is adapted to reverse one of the two or more applied electrical power sources. Alternatively, the switching means is adapted to cause one electrical power source to modulate the other or another. The switching means may also be adapted to pulse one or each electrical power source.

A third aspect of the invention is the provision of an electrolyte for enhancing the process as operated in accordance with the invention, the electrolyte comprising at least two organic additives, at least one being a polariser the effects of which are inhibited by reverse voltages, and the other being a depolariser that is preferentially adsorbed.

A basic arrangement of equipment in accordance with the invention is shown diagrammatically in Figure 4(a) of the accompanying drawings. There are two variable-voltage

sources or supplies 7 and 8 each connected to a control unit 9, which contains a number of solid-state switching devices capable of connecting a pair of conductors 10 leading to the cell 4 to either of the supplies or of isolating them. Alternatively the unit 9 switches in the source 8 to modulate the output from source 7. Figure 5 shows a typical control arrangement for such a unit.

Similar control could be produced by using known electrical devices or circuits which dissipate some of an input voltage to produce a lower value, but this would only be convenient for instruments or other applications of the invention using a low current; at typical electroplating currents, the power lost would be difficult to dispose of.

Typical effects produced are shown in the further time-base graphs of Figures 4(b) and 4(c), the former showing both forward and reverse voltages being pulsed, and the latter showing simple reversal for a lesser time but with a higher reverse voltage.

The control unit is normally capable of producing pulses of frequency and mark-space ratio which are independently adjustable for each supply and for adjustable periods before switching from one to another. The programme may provide for more than one such setting for either or both supplies. Several different voltages may be applied to the cell in each direction, in which case the control unit may need to provide for connection to more than two power supplies. An example of the use of such a facility would be a requirement for the pulsed voltage to fall not to zero but to some other value during each pulse. The settings of the

control unit or the voltages of the power supplies may be arranged to vary with time or with total current passed so as to provide optimum conditions at various stages of a process.

A typical application for the system disclosed is the production of printed circuit boards by deposition of acid copper from an acid electrolyte. Electrodeposited copper is used to provide electrical conduction in through holes used for component connection and for connection between surfaces and intermediate layers.

The conventional process employs an aqueous electrolyte of copper sulphate and sulphuric acid to which are usually added chloride ions and organic additives to assist with anode dissolution and to give deposits with suitable mechanical properties. The current distribution on many boards makes it very difficult to deposit sufficient copper on some parts of the board, eg. high aspect ratio through holes, without excessive thicknesses on other areas, eg. fine tracks and isolated pads. This in itself causes problems with dry film solder resists applied at a subsequent stage.

Therefore, when operating an improved electrodeposition process in accordance with the invention using independently-variable forward and reverse voltages, the electrolyte comprises an acid copper sulphate solution containing high molecular weight polyethers, sulphur propyl sulphides and chloride ions which together change the polarisation characteristics of the solution at different current densities thus effecting an improvement in the distribution of copper over complex shapes such as printed circuit boards.

It is true that the above additives, singly or together, have little or no beneficial effect on the distribution of copper when using direct current. It is also true that singly these additives have no effect on distribution when using pulsed or differential pulse reverse current.

Using the conventional process with uni-directional voltage at low current density the polarisation of the cathode is primarily effected by adsorption of the polyether and sulphide. As the current density increases diffusion effects of the sulphide become dominant. Using independently-variable forward and reverse voltages with pulses with precisely controlled length, frequency and amplitude, the diffusion process is blocked at higher current densities. The polyether has an inhibiting effect on the deposition of copper and the sulphide has a depolarising (stimulating) effect which is therefore diminished at higher current density areas giving an overall improvement in metal distribution.

The acid copper solution which forms part of the invention preferably contains:

Copper Sulphate 10 - 350 g/l

Free Acid 100 - 350 g/l

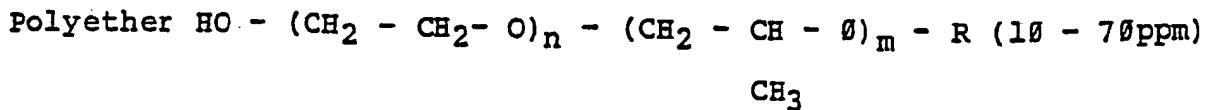
Chloride ion 40 - 400 ppm

A compound of general formula R - $(CH_2)_n - SO_3X$ (10 - 40 ppm)

where n is an integer between 2 and 4

X is hydrogen or an alkali metal

R is a sulphur containing group eg. mercapto propane sulphonic acid



where n and m are integers whose combined values give a total molecular weight of 1000 to 50000
R is hydrogen or a hydrophobic group.

Example 1

The following additives were added to an acid copper sulphate bath.

70 ppm Oxylube 200

40 ppm Mercapto propane sulphonic acid

100 ppm Chloride (as hydrochloric acid)

Two Hull cell panels were plated as follows:

Panel 1.

Uni-directional voltage at 2 amps for 10 minutes.

Panel 2.

Independently-variable reversed voltages applied for a total of 10 minutes, i.e., forward at 2 amps for 10 msec. and reverse at 7 amps for 0.5 msec.

Using a coulometric technique the copper thickness was measured at 1cm intervals across each panel. The results are shown graphically in Figure 6.

Example 2

In the same solution as that used in Example 1 sample printed circuit panels 3.2mm thick with plated through holes of 0.5mm diameter were plated as follows:-

Panel 1.

Uni-directional voltage at 3 amps/Dm for 45 minutes.

Panel 2.

Independently-variable reversed voltages applied for a total

of 45 minutes, i.e., forward at 3 amps/Dm for 10 msec. and reverse at 5 amps/Dm for 1 msec.

Copper Thickness (microns)

	<u>Surface</u>	<u>Hole</u>
Panel 1.	27	13
Panel 2.	23	27

CLAIMS

1. A method of operating an electrochemical process comprising the application of at least two independently-controlled voltages in alternation.
- 2: A method as in Claim 1, wherein more than two independently-controlled voltages are applied cyclicly.
3. A method as in Claim 1 or Claim 2, wherein one of the voltages is reversed.
4. A method as in Claim 1 or Claim 2, wherein one of the voltages modulates the other or another voltage.
5. A method as in any one of Claims 1 to 4, wherein one or each voltage is pulsed.
6. Equipment for operating an electrochemical process comprising at least two independently-controlled electrical power sources and switching means for applying them in alternation.
7. Equipment as in Claim 6, wherein the switching means is adapted to apply more than two independently-controlled voltages cyclicly.
8. Equipment as in Claim 6 or Claim 7, wherein the switching means is adapted to reverse one of the two or more applied electrical power sources.
9. Equipment as in Claim 6 or Claim 7, wherein the switching means is adapted to cause one electrical power source to modulate the other or another.
10. Equipment as in any one of Claims 6 to 9, wherein the switching means is adapted to pulse one or each electrical power source.
11. A method as in Claim 3 applied to an

electrodeposition process, wherein the electrolyte comprises at least two organic additives, at least one being a polariser the effects of which are inhibited by reverse voltages, and the other being a depolariser that is preferentially adsorbed.

12. A method as in Claim 11, wherein the electrolyte comprises an acid copper sulphate solution containing high molecular weight polyethers, sulphur propyl sulphides and chloride ions which together change the polarisation characteristics of the solution at different current densities thus effecting an improvement in the distribution of copper over complex shapes such as printed circuit boards.

13. A method as in Claim 12, wherein the acid copper solution contains:

Copper Sulphate 10 - 350 g/l

Free Acid 100 - 350 g/l

Chloride ion 40 - 400 ppm

A compound of general formula R - $(CH_2)_n - SO_3X$ (10 - 40 ppm)

where n is an integer between 2 and 4

X is hydrogen or an alkali metal

R is a sulphur containing group eg. mercapto propane sulphonic acid

Polyether HO - $(CH_2 - CH_2 - O)_n - (CH_2 - CH - O)_m - R$ (10 - 70 ppm)

CH_3

where n and m are integers whose combined values give a total molecular weight of 1000 to 5000

R is hydrogen or a hydrophobic group.

14. A method as in Example 1 as applied to Panel 2.

15. A method as in Example 2 as applied to Panel 2.

AMENDED CLAIMS

[received by the International Bureau on 24 July 1989 (24.07.89)
original claims 1,3 and 11 replaced by amended claim 1; original claims 2,4 and 5 replaced
by amended claims 2-4; claims 12-15 replaced by amended claims 5-8 (2 pages)]

1. A method of operating an electrochemical process comprising the application of at least two independently-controlled voltages in alternation, wherein one of the voltages is reversed, and wherein the electrolyte comprises at least two organic additives, at least one being a polariser the effects of which are inhibited by reverse voltages, and the other being a depolariser that is preferentially adsorbed.

2. A method as in Claim 1, wherein more than two independently-controlled voltages are supplied cyclicly.

3. A method as in Claim 1, wherein one of the voltages modulates the other or another voltage.

4. A method as in any one of Claims 1 to 3, wherein one or each voltage is pulsed.

5. A method as in any one of Claims 1 to 4, wherein the electrolyte comprises an acid copper sulphate solution containing high molecular weight polyethers, sulphur propyl sulphides and chloride ions which together change the polarisation characteristics of the solution at different current densities thus effecting an improvement in the distribution of copper over complex shapes such as printed circuit boards.

6. A method as in Claim 5, wherein the acid copper solution contains:

Copper Sulphate 10 - 350 g/l

Free Acid 100 - 350 g/l

Chloride ion 40 - 400 ppm

A compound of general formula R - (CH₂)_n - SO₃X (10 - 40 ppm)

where n is an integer between 2 and 4

X is hydrogen or an alkali metal

R is a sulphur containing group eg. mercapto propane sulphonic acid

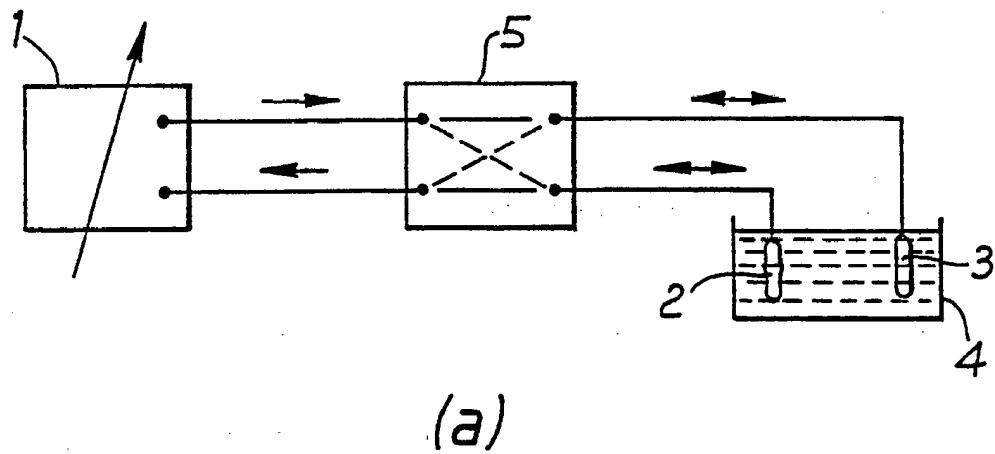
Polyether HO - (CH₂ - CH₂ - O)_n - (CH₂ - CH - Θ)_m - R (10 - 70 ppm)
CH₃

where n and m are integers whose combined values give a total molecular weight of 1000 to 5000

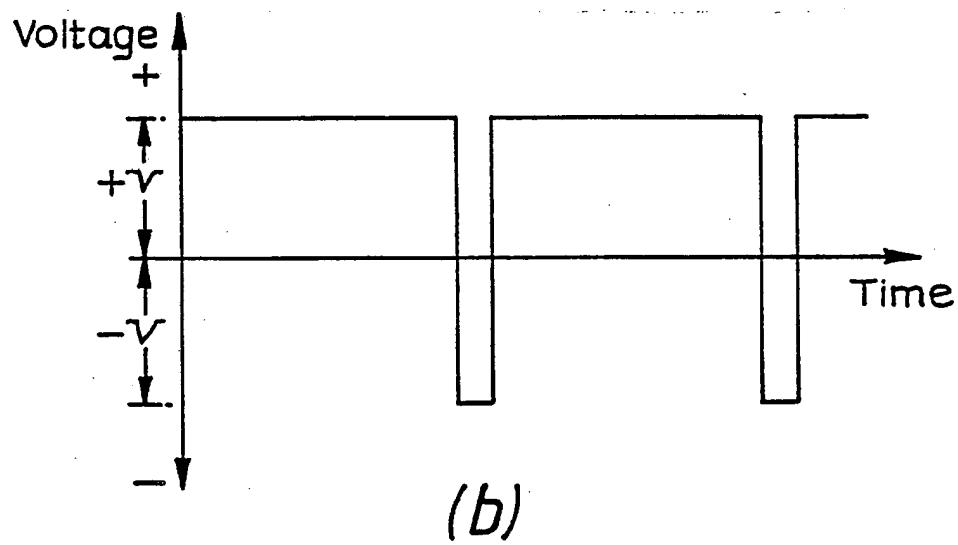
R is hydrogen or a hydrophobic group.

7. A method as in Example 1 as applied to Panel 2.
8. A method as in Example 2 as applied to Panel 2.

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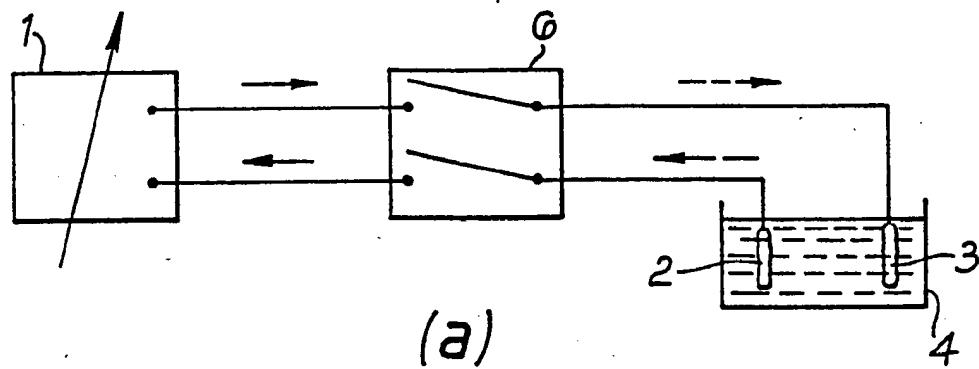
(a)



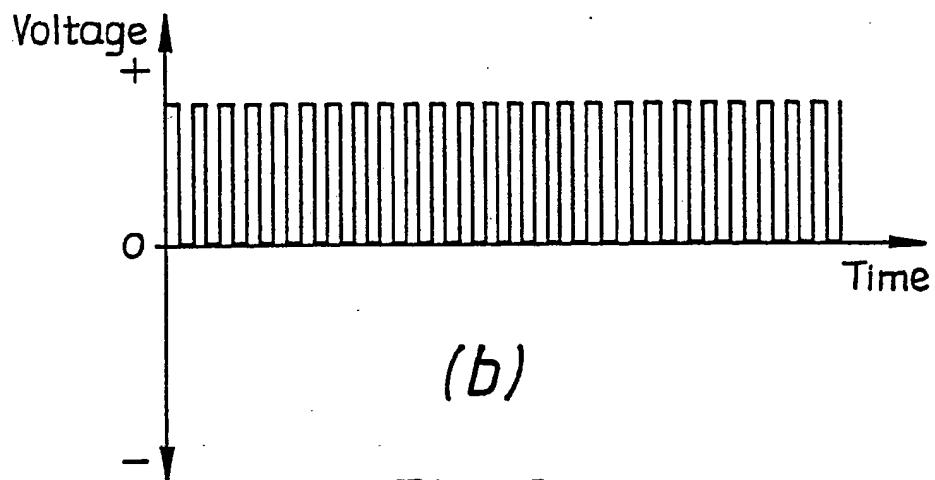
(b)

Fig. 1

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(a)



(b)

Fig. 2

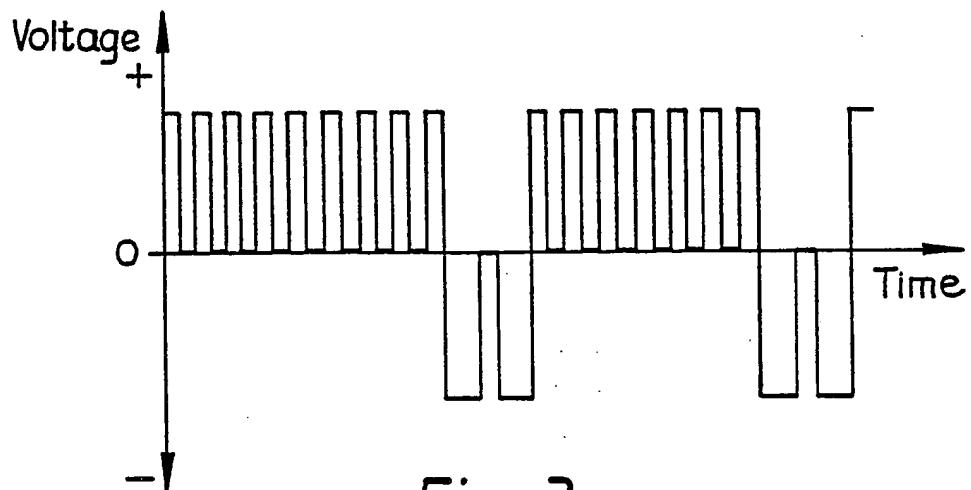


Fig. 3

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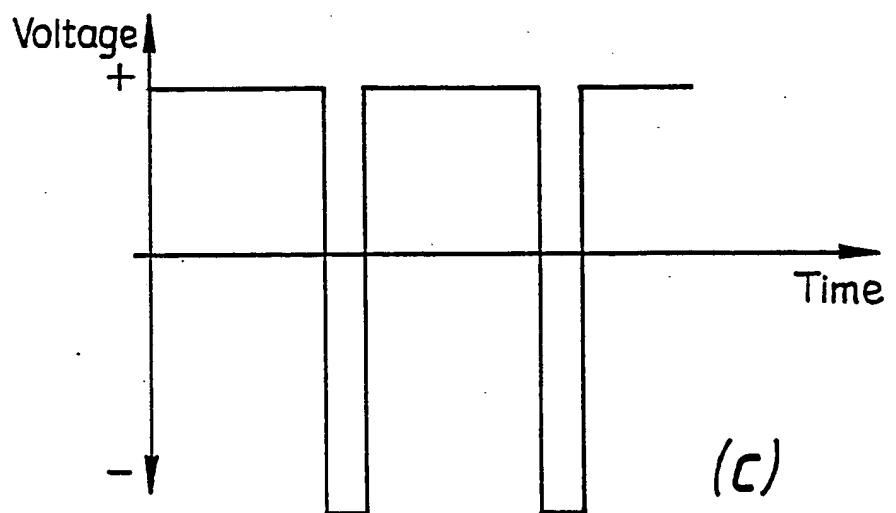
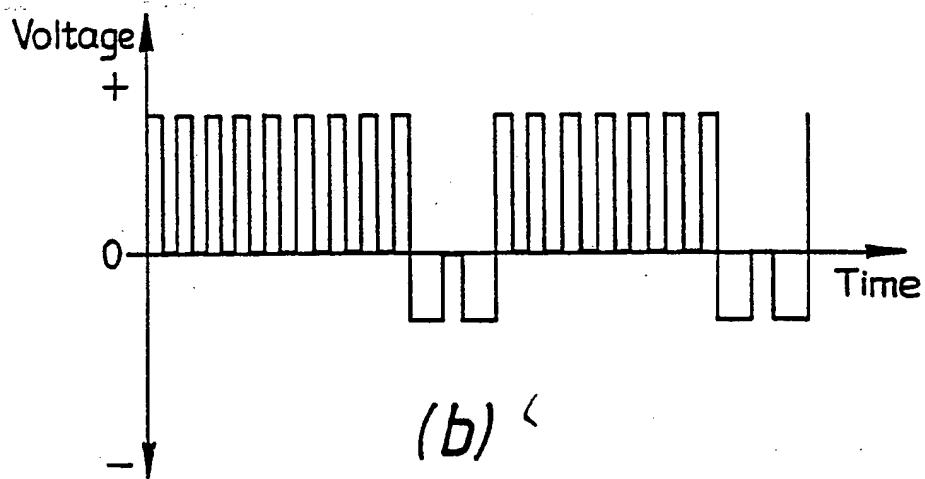
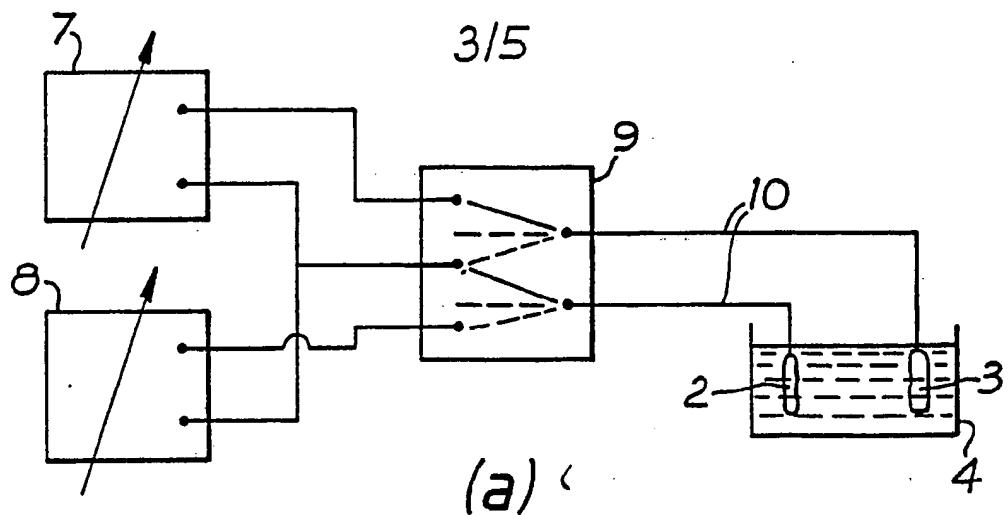


Fig. 4

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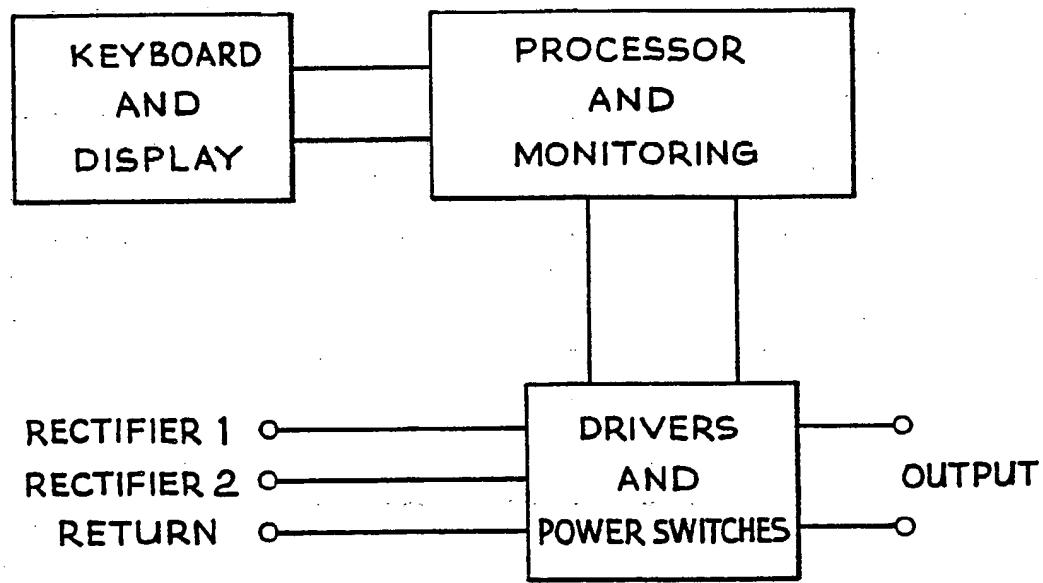


Fig. 5

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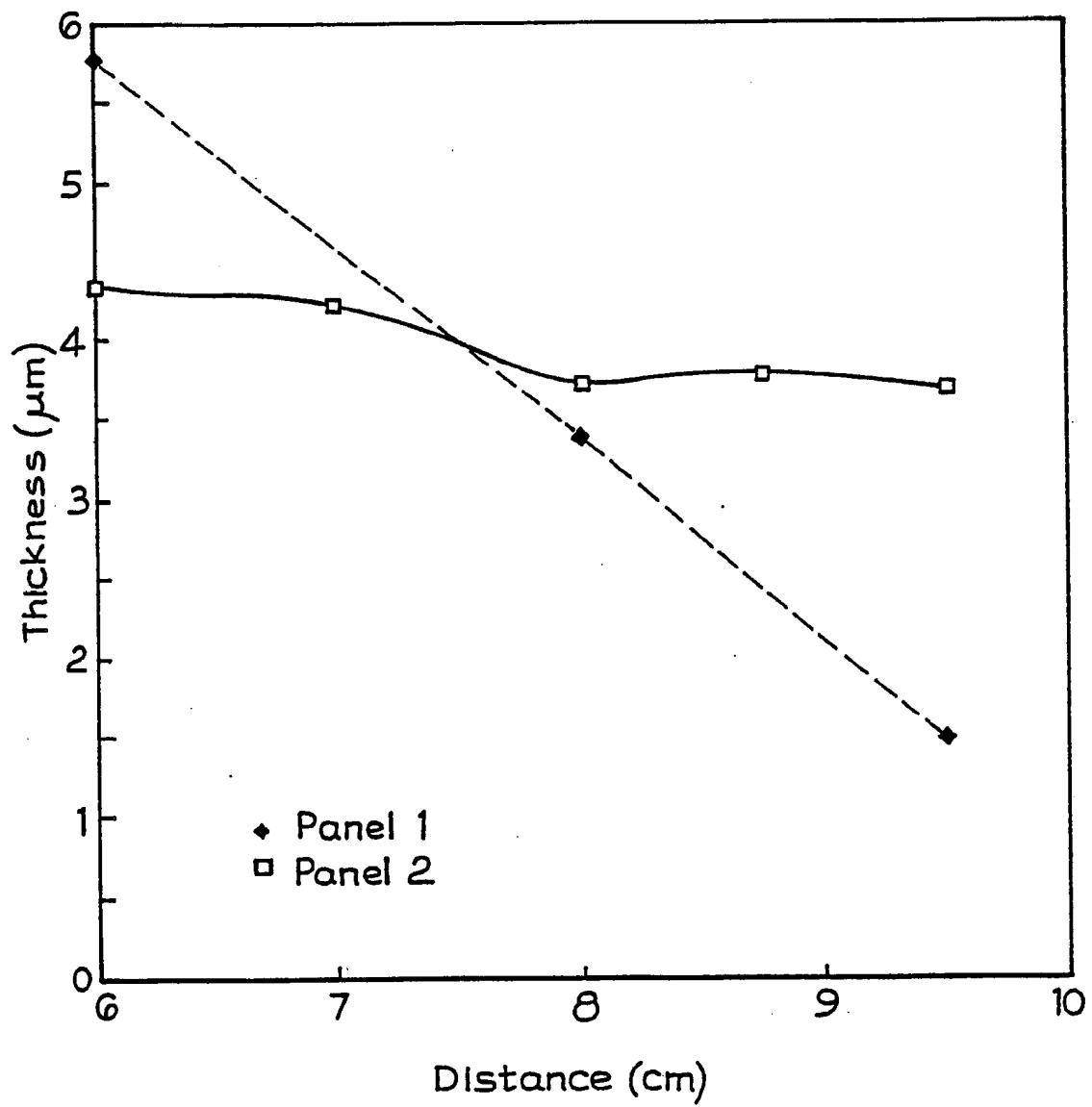
Thickness v. Distance on Hull Cell Panel

Fig. 6

SUBSTITUTE SHEET

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/GB 89/00042

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) *

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC⁴: C 25 D 5/18; C 25 D 3/38

II. FIELDS SEARCHED

Minimum Documentation Searched ⁷

Classification System	Classification Symbols
IPC ⁴	C 25 D 5/18

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched *

III. DOCUMENTS CONSIDERED TO BE RELEVANT*

Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	US, A, 4466864 (BACON) 21 August 1984 see column 4, lines 54-68; column 5, lines 55-60; column 6, lines 3,17-23 --	1-11
X	US, A, 4517059 (LOCH) 14 May 1985 see column 1, lines 1-2; column 3, lines 60-62; column 9, lines 55-58; column 13, lines 40-51; claims --	1-11
A	Plating and Surface Finishing, volume 73, no. 3, March 1986, (Orlando, Florida, US), N.M. Osero: "An overview of pulse plating", pages 20-22 --	1-11
A	GB, A, 779906 (ELECTRO-CHEMICAL ENGINEERING CO.) 24 July 1957 see page 2, lines 57-90 --	1-11
A	US, A, 3328273 (CREUTZ) 27 June 1967 --	11-13 ./.

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"G" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

29th April 1989

Date of Mailing of this International Search Report

30.05.89

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

M. VAN MOL

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category*	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
	see column 2, lines 1-34; column 4, lines 21-75 --	
A	GB, A, 2159539 (OMI) 4 December 1985 see page 5, line 10; claims -----	11-13

ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.

GB 8900042
SA 26456

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 24/05/89. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A- 4466864	21-08-84	None		
US-A- 4517059	14-05-85	None		
GB-A- 779906		None		
US-A- 3328273		None		
GB-A- 2159539	04-12-85	US-A- 4555315 AU-B- 564519 AU-A- 4307385 DE-A- 3518193 FR-A- 2565259 JP-A- 61041787	26-11-85 13-08-87 05-12-85 05-12-85 06-12-85 28-02-86	